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Grain boundary diffusion in oxides and its contribution to oxidation processes

A Atkinson

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GRAIN BOUNDARY DIFFUSION IN OXIDES AND ITS CONTRIBUTION
TO OXIDATION PROCESSES

A. Atkinson

Abstract

Experimental data for the preferential diffusion of species along grain boundaries in oxides, relevant to oxidation films, are briefly reviewed and discussed in terms of the likely atomistic processes responsible for diffusion.

The data are then used to assess the contribution of grain boundary diffusion to oxidation processes such as film growth, the distribution of impurities and the influence of impurities on film growth in the oxidation of nickel based systems (Ni, Ni-T, Ni-CeO₂, Ni-Cr).

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Introduction

Grain boundaries and dislocations are potential routes for rapid (or short-circuit) diffusion in crystalline materials because there is usually greater disorder in the arrangement of atoms within these regions than in the bulk lattice. (Conversely, in materials which have highly disordered bulk lattices, grain boundaries and dislocations will not enhance transport; indeed, they may even reduce it.) The relative importance of short-circuit transport, compared to bulk lattice transport, will generally be greater for lower temperatures, smaller grain sizes and materials which tend to contain low concentrations of lattice defects. These conditions are all found in oxide films growing on corrosion resistant alloys in service conditions. It is therefore to be expected that many of the key processes which involve material transport in oxide films will be controlled by short-circuit diffusion along grain boundaries and/or dislocations.

The most obvious process which is likely to be controlled by short-circuit diffusion is the rate at which the oxide film grows, by metal ions diffusing outwards and/or oxide ions diffusing inwards. But, there are several other important processes taking place during oxidation which involve material transport and they are all potentially interdependent. For example, the microstructure in the film will depend on the film growth mechanism which will in turn depend on the microstructure. This is particularly so in alloy oxidation where the location of alloying elements, which can influence diffusion and oxide grain size, is controlled by the diffusion of the alloying elements in the oxide film. The generation of stress in a growing film may also be diffusion controlled, e.g. by the reaction of metal ions and oxide ions diffusing in opposite directions within the film. The response of the film to these stresses can also be determined by diffusion-controlled creep processes. Finally, the ability of an oxide film to protect the metal from attack by more aggressive constituents in the environment (e.g. sulphur) may also be determined by diffusion.

In order to assess the contribution that short-circuit diffusion can make to such processes it is clearly necessary to know the magnitude of some key short-circuit diffusion coefficients and how they may be influenced by other parameters. In particular, it would be useful to know the short-circuit diffusion coefficients of some metals and oxygen in important oxides, how they are influenced by impurities and what atomic processes are responsible. Some of these goals have now been achieved for NiO, which is a convenient model material for oxides which grow as corrosion-resistant films. The aim of this paper is to show how such an approach can be used to try and improve understanding of some oxidation processes. We first survey briefly what is currently known about short-circuit diffusion (self diffusion, impurity diffusion and influence of impurities) in oxides and then we apply this to some oxidation processes involving NiO. These are growth rate of NiO films, growth rate and microstructure of NiO on CeO₂-coated Ni and the oxidation rate and microstructure of dilute Ni-Cr and Ni-Y alloys.

Grain Boundary and Dislocation Diffusion in Oxides

Self Diffusion

Data for self diffusion along short-circuits in oxides have been reviewed in a number of recent articles (1,2,3). The available experimental data are not extensive, but they are sufficient for some detailed observations to be made for NiO and some tentative generalisations extended

to other oxides. Data for both Ni and O diffusion along dislocations and grain boundaries in NiO are presented in Fig. 1 compared with the corresponding lattice diffusion coefficients. In the case of grain boundary diffusion the actual parameter measured experimentally is the product, $D'\delta$, of the grain boundary diffusion coefficient and boundary width. In the case of dislocations it is the same parameter measured for a low angle boundary. If the mean separation of dislocations in the low angle boundaries is known then the parameter $D_g a^2$ can be deduced, where D_g is the dislocation diffusion coefficient and a is the effective radius of the dislocation assuming it to be approximated as a cylindrical pipe. For estimations of material transport these combined parameters are the relevant ones. However, in order to compare actual diffusion coefficients the geometrical parameters δ and a must also be measured. Experiments have been carried out (3,4) to obtain a rough estimate of δ and a at a single temperature (in this case approximately 400°C). These experiments showed that both the width of the

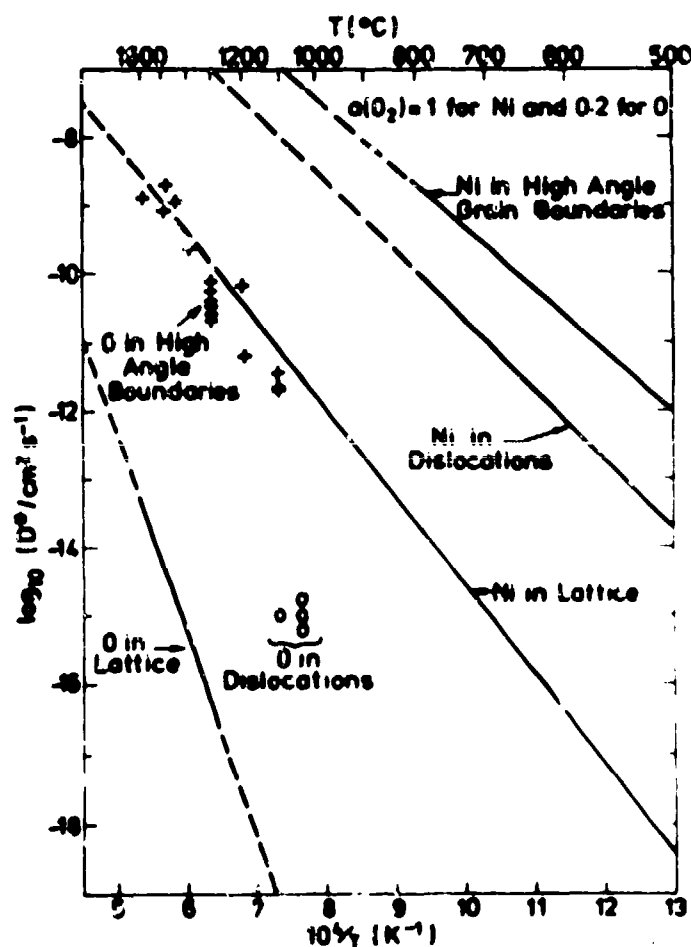


Figure 1 - Diffusion coefficients of Ni and O in the lattice, in dislocations and along grain boundaries in NiO. The oxygen pressure was 1 atm for Ni diffusion and 0.2 atm for O. The dislocation diameter and grain boundary width have both been assumed equal to 1 nm (4,5,13,14).

grain boundary and the diameter of the dislocation are approximately 1 nm in NiO. Thus the fast-diffusivity region is essentially confined to the core of the boundary or dislocation and no significant contribution is made by the space charge region which surrounds the boundary in ionic materials. In Fig. 1 it has therefore been assumed that $\delta = 2r = 1$ nm.

These data illustrate several important features of short-circuit diffusion. First, dislocations and grain boundaries are very similar. This is to be expected since theoretical models of grain boundary structures show atomic configurations which are similar to those predicted for isolated dislocations (6,7). Second, the diffusivities of both metal and oxygen are enhanced in the boundary with respect to the corresponding lattice diffusivities, but their relative order is maintained, i.e. the faster diffuser in the lattice is also the faster in the boundary. Third, the degree of enhancement can be very great (a factor of 10^3 is typical) and the activation energies for short-circuit diffusion are significantly lower than for bulk diffusion, as summarised in Table 1.

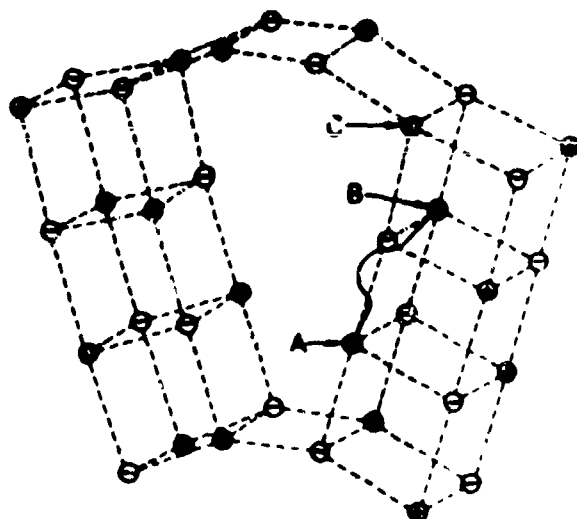
Table 1. Activation Energies, Q (eV), for Grain Boundary Diffusion in NiO (11)

	Experiment			Calculation		
	Q_{gb}	Q_L	$\frac{Q_{gb}}{Q_L}$	Q_{gb}	Q_L	$\frac{Q_{gb}}{Q_L}$
Ni Diffusion	1.78	2.56	0.70	1.6-2.2	2.9	0.3-0.3
O Diffusion	2.3	5.6	0.45	2.5	5.3	0.47

The influence of grain boundary misorientation on grain boundary diffusion is not well-established in oxides (or in metals). The data for Ni in NiO show that there is some difference between 'low angle' and 'high angle' boundaries and Osenbach and Stubican (8) showed that Cr diffusion in [100] tilt boundaries in NiO increased with tilt angle as expected for a dislocation model of such boundaries. Experiments of this type have been much more extensive in metals, but have not produced conclusive results (2,9). At present it appears that grain boundary diffusion in most high angle boundaries is not sensitive to boundary misorientation except in some special cases such as the (111)/[011] coherent twin boundary in fcc materials. (In this notation the first index is the boundary plane and the second the direction about which the two crystals have been symmetrically tilted.)

Although there are no direct experiments which allow the mechanism of grain boundary (or dislocation) diffusion to be identified there is now a body of indirect evidence, from both experiment and theory, to support the concept that a point defect is involved which is similar to a lattice defect (e.g. vacancy or interstitial). In NiO, an increase in oxygen activity, a_{O_2} , leads to an increase in the concentration of vacant Ni sites and hence an increase in the lattice diffusion coefficient for Ni. It is also found (4,5) that grain boundary and dislocation diffusion of Ni in NiO increases in a similar way. This may be explained if grain boundary diffusion of Ni in NiO also occurs by a nickel vacancy whose concentration and mobility is greater in the boundary than in the lattice. Similar behaviour has also been reported for Cr diffusion along dislocations (as low angle boundaries) in Cr_2O_3 (10).

This concept is supported by theoretical studies of the structure and properties of grain boundaries in NiO (7,11) and dislocations in MgO (12). The calculated structure of the (310)/[001] 36.9° tilt boundary in NiO is shown schematically in Fig. 2 (11). The structure has relatively open channels parallel to the tilt axis and easy diffusion along this direction is thus expected. Burdett and Tashir have calculated the energies required to form defects ($V_{Ni}^{''}$, $V_O^{''}$, $O_i^{''}$ and i) at various sites in simple boundaries of this type. They found that in all the boundaries which they considered there was always a site available for each defect in the boundary which reduced the energy of formation of the defect with respect to the corresponding bulk lattice defect. For example, in the case of the nickel vacancy its most stable location in the boundary shown in Fig. 2 is the site marked A. They studied the grain boundary diffusion process by calculating the lowest energy path a neighbouring nickel ion could take to move the vacancy to the next site along the boundary. In this example, the next site is labelled B and the predicted diffusion path is the curve linking A and B. A similar jump moves the vacancy to the next equivalent A site. This calculation was carried out for Ni diffusion along four different boundaries by a vacancy mechanism and for O diffusion along a single boundary by an interstitialcy mechanism. The results are summarized in Table 1 and compared with the measured activation energies for Ni and O grain boundary diffusion in NiO. The agreement between the measured and calculated values is very good, but may be fortuitous considering the approximations and uncertainties involved (particularly for O diffusion). However, the predicted ratio of the activation energies for grain boundary and lattice diffusion is also in very good agreement with the experimental value for both Ni and O, and this should be less sensitive to errors than the absolute value. Of necessity, the calculations were only carried out for a few highly symmetric boundaries and a limited range of possible



(310)/[001] NiO tilt boundary.

Figure 2 - Calculated structure of the (310)/[001] 36.9° symmetrical tilt boundary in NiO showing the path taken by a nickel ion during its easy diffusion parallel to the tilt axis. The ions are not drawn to realistic relative size (11).

diffusion pathways. Nevertheless, the broad agreement with the measured self-diffusion properties of more general boundaries which were present in the polycrystalline specimens gives confidence in extending this approach to the prediction of other properties of grain boundaries (such as the behaviour of segregated impurities); at least at a qualitative level.

Impurity Diffusion

The diffusion of Co, Cr and Ce in NiO grain boundaries in polycrystalline NiO specimens, similar to those used for self-diffusion studies, has recently been studied (15). These ions are expected to be in charge states Co^{2+} , Cr^{3+} and Ce^{4+} and therefore represent a reasonable cross section of impurity behaviour. For example, they differ widely in their solubility and segregation characteristics. Ce is completely soluble in the NiO lattice and should not segregate appreciably to grain boundaries. Co has negligible lattice solubility and will dissolve only at grain boundaries. Cr falls between these extremes, having slight lattice solubility and appreciable grain boundary segregation (16).

The measured grain boundary diffusion coefficients are summarised in Fig. 3 together with the corresponding lattice diffusion coefficients where appropriate. In the case of Co, it has been assumed that segregation to the boundary is negligible and that the boundary width is the same as for Ni diffusion (i.e. 1 nm). No assumptions were necessary for Ce since it is insoluble in the NiO lattice and therefore its diffusion coefficient in the boundary is measured directly. For Cr the experiments were analysed in a way which allowed the segregation and diffusion contributions to be separated in a self-consistent way (again assuming $\delta = 1$ nm). The diffusion coefficients are in the order $D_{\text{Co}} > D_{\text{Ni}} > D_{\text{Cr}}$ for both lattice and grain boundary diffusion (no comparison can be made for Ce because of its negligible lattice solubility), which reinforces the view that grain boundary and lattice diffusion both take place by a similar mechanism. The atomic characteristics that control impurity diffusion are not understood even for lattice diffusion (17), but ionic charge is obviously important since, in general, the higher the charge on the ion the more slowly does it tend to diffuse.

The Influence of Impurities on Self-Diffusion

The impurities which influence self-diffusion in the lattice most are those which have a different valency to the host ions. Thus a trivalent substitutional impurity in a divalent host would be expected to increase the concentration of oppositely charged defects (e.g. cation vacancies). Recently, several attempts have been made to study such doping effects on grain boundary diffusion in oxides. Chadwick and Taylor (18) measured the diffusion of Ni in NiO grain boundaries doped with Ce impurities. The polycrystalline specimens were produced by oxidising Ni in a similar way to those used by Atkinson and Taylor (5) and were doped by applying a CeO_2 coating to the Ni before oxidation. They found that the presence of Ce had no effect on grain boundary diffusion of Ni tracer.

Moosa et al. (19) have reported similar experiments performed on Y-doped polycrystalline NiO produced by oxidising Ni-0.1 wt.% Y alloy. They concluded that the presence of the yttrium had no significant influence on the grain boundary diffusion of Ni. Furthermore, their results on both undoped and Y-doped specimens were in good agreement with the earlier work of Atkinson and Taylor (5) on undoped NiO.

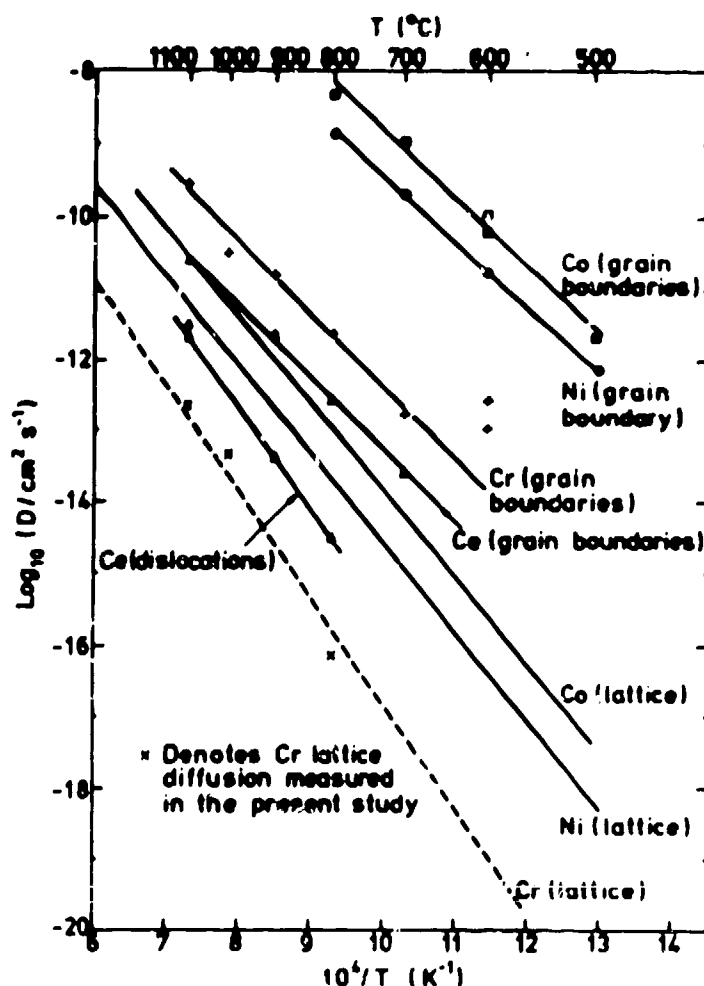


Figure 3 - Diffusion coefficients for some impurities in NiO grain boundaries (at an oxygen pressure of 1 atm) compared with the corresponding lattice diffusivities. The boundary width has been assumed equal to 1 nm and Co has been assumed to have negligible boundary segregation (15).

Whilst these studies of Co- and Y-doped materials appear to show that grain boundary diffusion is not sensitive to impurities, there are other experiments which indicate just the opposite. Experiments in which Ni diffusion has been studied along single boundaries in NiO bicrystals (20) have indicated that impurities such as Ca and Si, which have low lattice solubility and segregate strongly to the boundary, can either suppress or enhance grain boundary diffusion depending on the way in which the impurity is segregated at the boundary. More recently, we have attempted to measure the diffusion of Ni along grain boundaries in Cr-doped polycrystalline NiO (21). The specimens which were used were again prepared by oxidation of Ni alloy (Ni 0.1% Cr) at 1100°C. SIMS analysis revealed that the Cr/Ni ratio in the outer part of the film was about 0.03%. In these specimens the

Cr dopant blocked many of the boundaries to Ni diffusion. Moreover, those that were not completely blocked had a lower diffusivity for Ni than undoped boundaries as indicated in Fig. 4. The data in Fig. 4 show that Cr doping increases the diffusivity of Ni in the lattice (as expected from the compensating increase in the concentration of Ni vacancies), but decreases the diffusivity of Ni in grain boundaries (for temperatures below 900°C). In the light of these experiments it seems reasonable to question whether the boundaries in the Cr- and Y-doped specimens were really doped as expected. For example, Mason et al. (19) suggest that precipitation of the Y dopant may be the reason for its lack of influence on grain boundary diffusion in their experiments.

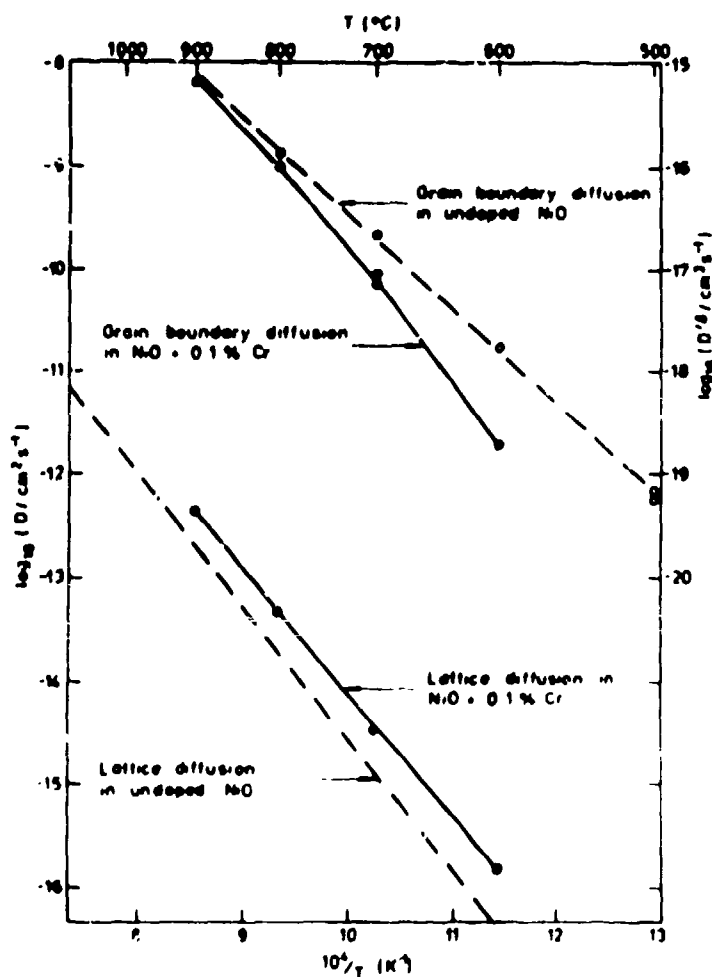
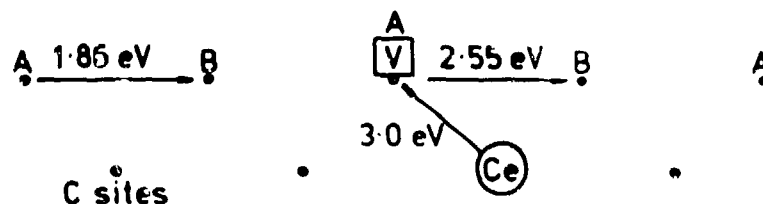


Figure 4 - The influence of Cr doping (approximately 0.1%) on the diffusion of Ni in the lattice and along grain boundaries in NiO. The Ni/Cr ratio on the grain boundaries is estimated to be about 2% (21).

In summary, therefore, it appears that contradictory results have been obtained concerning the influence of higher valency cations (e.g. Cr, Y, Ce) on the grain boundary diffusion of Ni in NiO. This is probably due to the difficulty in fabricating specimens and it may well be that diffusion is

blocked, provided that the impurity concentration is sufficiently high. In none of the experimental studies referred to here has it been possible to directly measure the concentration of dopant at the boundary. However, in the case of Cr the concentration can be inferred from the bulk concentration and the known segregation coefficient of Cr (15,16) at the temperature at which the specimens were fabricated (1150°C). On this basis the Cr/Ni ratio in the boundary in these experiments is estimated to be about 2%. This was apparently sufficient to block Ni diffusion, or slow it down as indicated in Fig. 4.

The mechanism by which a cation impurity with a charge greater than the host cation can increase lattice diffusion of the host but decrease grain boundary diffusion can be qualitatively understood with guidance from the modelling studies. Duffy and Tasker (11) have modelled the behaviour of substitutional Ce^{4+} ions in the (310)/[001] tilt boundary in NiO. They predict that although the Ce^{4+} ions will be compensated by an increased concentration of nickel vacancies there are strong interactions between these oppositely charged defects in the boundary which favour the formation of $(\text{Ce}_{\text{Ni}}, \text{V}_{\text{Ni}})^{\pm}$ pairs and larger ordered arrays of defects. The activation energy for the Ce and vacancy to exchange is estimated to be 3.0 eV whereas that for Ni-vacancy exchange in the same boundary is estimated to be 1.86 eV. This difference is in agreement with the experimental observation that grain boundary diffusivity of Ce is much less than Ni. In a Ce-doped boundary the charge-compensating vacancies can only contribute to long-range Ni diffusion if they can migrate past the effectively immobile Ce^{4+} ions. Duffy and Tasker estimate that the energy required to do this is 2.55 eV which is not only greater than the energy for vacancy hopping in the undoped boundary (1.86 eV), but also greater than that for vacancy hopping in the lattice (2.4 eV by the same calculation methods). Hence the picture that emerges is one in which the more highly charged relatively immobile impurity ion has a strong attraction for vacancies such that the easiest diffusion path past the impurity is by a detour through the lattice. This process is illustrated schematically in Fig. 5. The concentration of impurity which is required to block grain boundary diffusion can be estimated roughly as $\exp(-\Delta E_m/kT)$ where ΔE_m is the difference between the migration energy of the vacancy in the lattice and the undoped grain boundary (in this case about 0.5 eV). Hence, at 1000°C an impurity concentration of about 1% (cation fraction) would be expected to block Ni diffusion in NiO grain boundaries. This is consistent with the observed effect of about 2% Cr-doping of NiO boundaries.



Jump energies in the (310)/[001] boundary

Figure 5 - Schematic diagram illustrating how an impurity such as Ce^{4+} in substitutional sites near the boundary plane in NiO can block diffusion of Ni at the boundary. The labels correspond to sites in Fig. 2 and the energies are calculated for exchange jumps with a vacancy between these sites (11).

Growth Rate of 'Pure' Oxides

The growth rate of thick oxide films by lattice diffusion can be related to the self-diffusion coefficients of the oxide using Wagner's electrochemical theory of oxidation (22). It is found in practice (23), however, that the theory is valid only for oxides that have large deviations from stoichiometry (e.g. FeO, CoO) or some other oxides at sufficiently high temperature (e.g. NiO, Fe₃O₄). In most cases of technological importance corrosion is relatively slow which means either the interest is in more refractory oxides (e.g. Cr₂O₃, ZrO₂, Al₂O₃) or in less refractory oxides at lower temperatures (e.g. NiO, Fe₃O₄, Fe₂O₃, Cu₂O). Under these conditions it is found that Wagner's theory based on lattice diffusion always underestimates the oxidation rate, sometimes by many orders of magnitude (23). This is an important piece of indirect evidence for the dominant role of short-circuit diffusion paths during the growth of 'pure' oxides. (An alternative rationalisation could be that fast diffusion in refractory materials and at low temperatures is caused by impurities increasing lattice diffusion. Whilst impurities undoubtedly have had some influence on the oxidation studies they are not the main cause of fast diffusion because the parent oxide films grown in oxidation experiments contain fewer impurities than the oxides in which diffusion studies have been carried out). Further indirect evidence for short-circuit diffusion comes from the observation that oxidation rate at 'low' temperature depends on crystallographic orientation of the metal substrate and its degree of cold working (24,25). Such dependences are not predicted by Wagner's theory and they indicate that the oxide microstructure is influencing the diffusion of species through it.

The measurements of grain boundary diffusion in NiO have been used (25) to show that the oxidation of Ni at temperatures below about 1100°C is controlled by the outward diffusion of Ni along grain boundaries in the NiO film. This is summarised in Fig. 6 in which the measured parabolic rate constant for Ni oxidation ($k_p = X^2/t$, where X is film thickness) is compared with that predicted from grain boundary diffusion data for Ni in NiO. Grain boundary diffusion was included in Wagner's theory by using an effective diffusion coefficient given by

$$D_{\text{eff}} = D_1 + 2 \frac{(D_1 g)^{1/2}}{g} \quad (1)$$

where g is the grain size in the oxide normal to the growth direction. Also included in Fig. 6 is k_p expected for lattice diffusion alone. It can be seen that at the lower temperatures the measured k_p is typically 10³ times greater than that predicted from lattice diffusion, but within about a factor of 2 of that predicted from grain boundary diffusion.

The direct correspondence between oxidation rate and grain boundary diffusion has only been established for NiO because there are no grain boundary diffusion data for other relevant oxides. Nevertheless, the general conclusion may be tentatively made that the growth of slow growing crystalline oxides ($k_p \lesssim 10^{-10} \text{ cm}^2 \text{ s}^{-1}$) is controlled by grain boundary diffusion in the oxide.

Oxidation of Ni-Y Alloys and CeO₂-coated Ni

Small additions of some elements to an oxide film are known to have a beneficial effect in increasing the adherence of the oxide to the metal and/or the rate of oxidation (so-called 'rare earth effect'). Typical effective elements of this type are Y and Ce; particularly in the case of Cr₂O₃ and Al₂O₃ films. Recently two studies of this phenomenon have been

carried out in NiO; the oxidation of dilute Ni-Y alloys and Ni coated with CeO_2 .

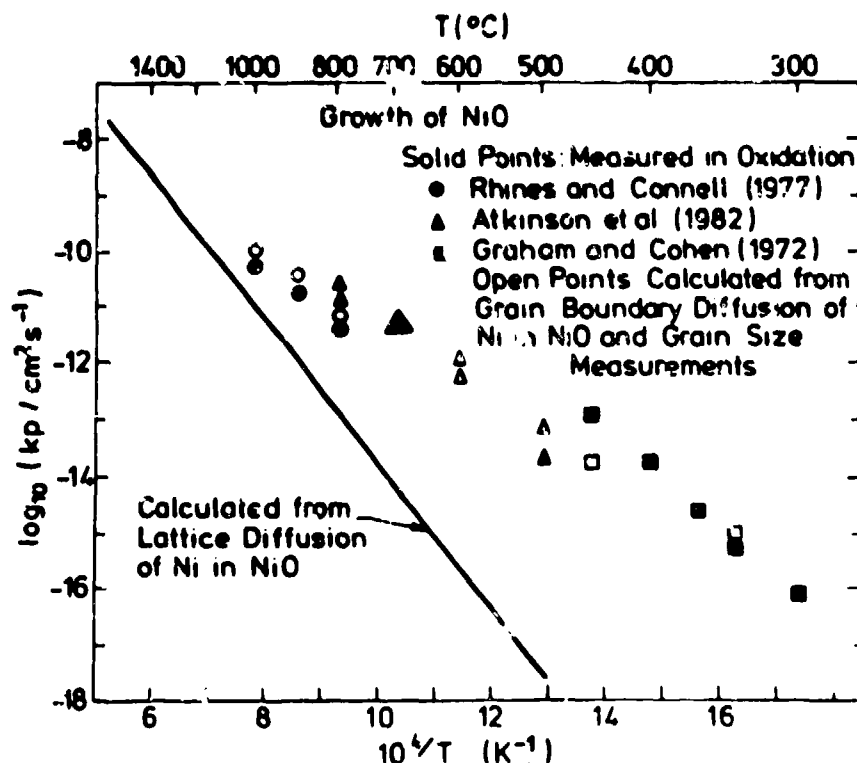


Figure 6 - Arrhenius plot of the parabolic rate constant for the oxidation of Ni to NiO. Solid points are directly measured values and open points are calculated using measured grain boundary diffusion coefficients and grain sizes. The solid line is the rate constant expected if lattice diffusion of Ni is the only diffusion process contributing to oxidation (26,27,28).

Oxidation of Ni-Y Alloys

Moosa and Rothman (29) measured the rate of oxidation of Ni, Ni-0.1 wt.% Y and Ni-0.3 wt.% Y alloys in oxygen at a pressure of 1 atm and at temperatures in the range 500-900°C. They found that Y increased the oxidation rate at 500 and 600°C, but decreased it at 700-900°C. The main influence of Y on the microstructure of the NiO film was found to be on the grain size of the NiO. At 500 and 600°C Y reduced the grain size, but increased the grain size at 700-900°C. Moosa and Rothman showed that the different grain sizes were able to account for the relative oxidation rates of Ni and the Ni-Y alloys. It was not necessary to assume that Y had any influence on grain boundary diffusion of Ni which is consistent with their diffusion measurements in Y-doped NiO. However, this behaviour is not consistent with the theoretical modelling which suggests that a trivalent substitutional ion such as Y^{3+} in NiO should block grain boundary diffusion

if present on the boundaries at sufficiently high concentration (e.g. above about 1%). In the absence of detailed microstructural investigations it is not known how the Y is distributed within the NiO film, particularly at grain boundaries. Thus it is possible to reconcile both expectations and observations if the Y in the film is present as relatively large well-separated Y-rich second phases as suggested by Moon and Rothman.

Oxidation of CeO₂-coated Ni

When CeO₂ is applied as a thin coating on Ni it greatly reduces the rate of subsequent Ni oxidation at temperatures below about 1100°C. This system has been studied in considerable detail by Chadwick and Taylor (30-31) and, more recently by Moon (33). The CeO₂ in these studies was applied to the Ni surface as a sol coating corresponding to a CeO₂ layer approximately 0.1 μm in thickness. The parabolic rate constant for NiO growth is reduced considerably by this treatment as illustrated in Fig. 7. At 700°C the rate is decreased by almost two orders of magnitude. The mature microstructure of the resulting composite film is illustrated schematically in Fig. 8. It consists of three distinct layers. The outermost columnar layer is almost pure NiO with a grain size similar to that of an undoped NiO film of the same thickness. Chadwick and Taylor (30) were able to detect some Ce at grain boundaries in this outer layer by SIMS. The innermost layer is similar to the outermost layer, but not as thick. The middle layer is a fine-grained, two phase mixture of NiO and CeO₂.

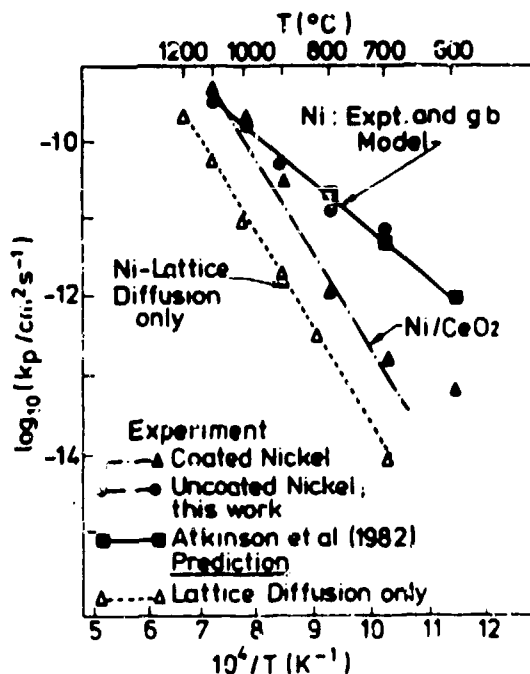


Figure 7 - The parabolic rate constant for the oxidation of CeO₂-coated Ni compared with that of pure Ni and that expected for NiO growth being controlled by lattice diffusion of Ni (30).

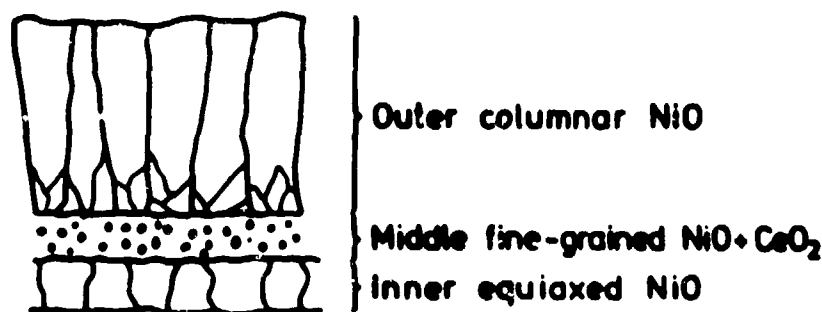


Figure 8 - Schematic diagram showing the mature microstructure of the oxide formed by oxidation of CeO_2 -coated Ni.

At first it was thought that the oxidation rate was controlled by the outer layer and that the Ce present on grain boundaries in the outer layer was reducing grain boundary diffusion. However, the tracer diffusion coefficient of Ni in these boundaries was found to be the same as in undoped NiO boundaries (Section 2.3). Furthermore, Chadwick and Taylor (31) showed conclusively (by an experiment in which a taper section through the film was re-oxidised) that it is in fact the middle, two-phase layer which controls the rate of oxidation. (This observation is consistent with the diffusion experiments which showed that Ce had no effect on grain boundary diffusion in the outer layer.) The rate of oxidation can be accounted for if it is assumed that there is no grain boundary diffusion within the two phase layer. Since the grain size in this layer is typically an order of magnitude smaller than in the other layers, the inference is that all the grain boundaries in the middle layer are ineffective as fast diffusion paths. Chadwick and Taylor (32) also observed that the outer layer had a strong preferred orientation; with $\langle 001 \rangle$ directions parallel to the growth direction. This led them to propose that the CeO_2 may lead to a predominance of low diffusivity boundaries having 'special' misorientation. Detailed microstructural analysis of grain boundary geometries, however, revealed that there was no significant bias towards 'special' boundaries in either the middle or outer layers (32).

It now appears that the original hypothesis in which Ce at NiO grain boundaries blocks grain boundary diffusion may after all be correct. Moon (33) has carried out a comprehensive microanalytical study of grain boundaries in (or near) the middle layer using STEM and has found that almost all the boundaries in this region have Ce at their cores (Fig. 9). The concentration of Ce at the boundaries in the middle layer (assuming $\delta = 1 \text{ nm}$) is equivalent to a Ce/Ni ratio of between 3 and 10%. From both the theoretical modelling and the observed influence of Cr on Ni grain boundary diffusion, this concentration of Ce is expected to be sufficient to block grain boundary diffusion, which is consistent with the oxidation experiments.

We must now explain why the Ce on the boundaries in the outer layer does not block Ni diffusion. There appear to be several contributing factors. First, Moon has observed that only about one in four of the boundaries in the outer layer had detectable Ce in it. Second, the

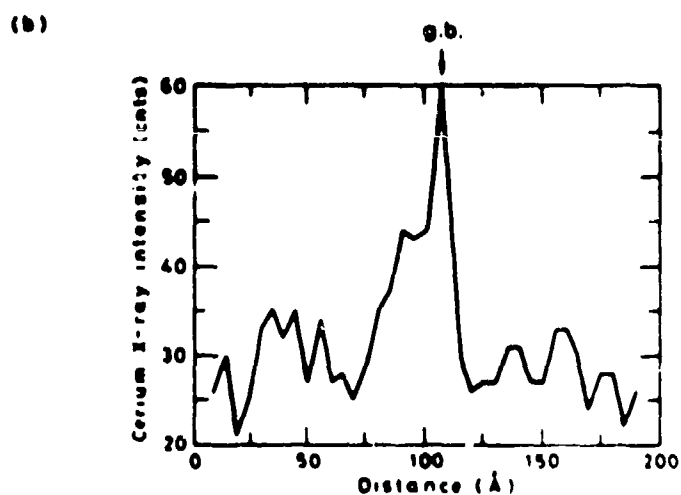
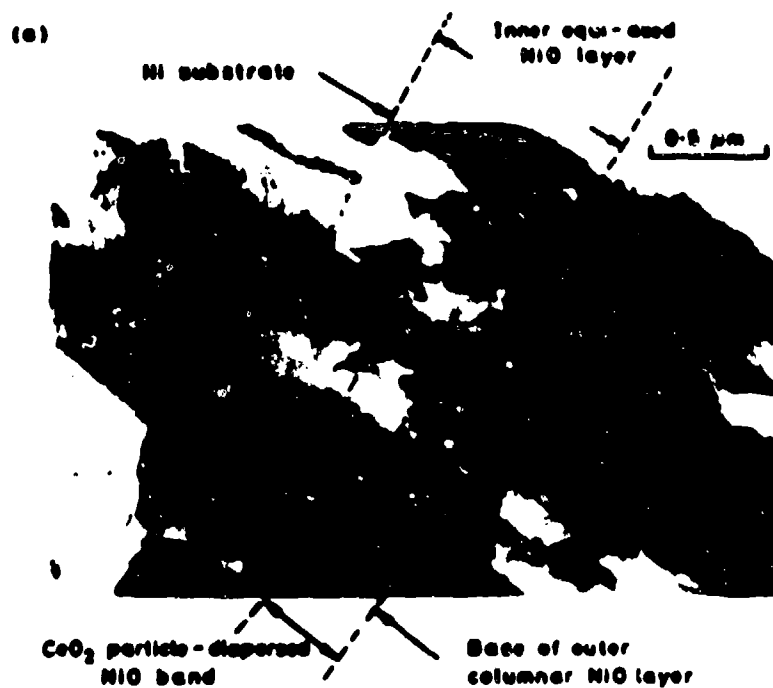


Figure 9 - (a) Bright-field transmission electron micrograph of a transverse section of nickel oxide scale formed on ceria-coated nickel (253 hrs, 900°C, O_2). (b) Profile of X-ray intensity for Ce across a grain boundary in the outer NiO layer, showing the presence of ~ 0.3 monolayers of segregated cerium at 0.3 μm distance from the ceria-rich layer (33).

concentration of Co in a boundary at the outer surface of the film is expected to be only about 2% of its maximum value (in the middle layer) because of the low grain boundary diffusion coefficient of Co (14). Third, the concentration of Co at grain boundaries in the inner layer is probably greater than its solubility limit in equilibrium with CoO_2 because of the high curvature of the small CoO_2 particles.

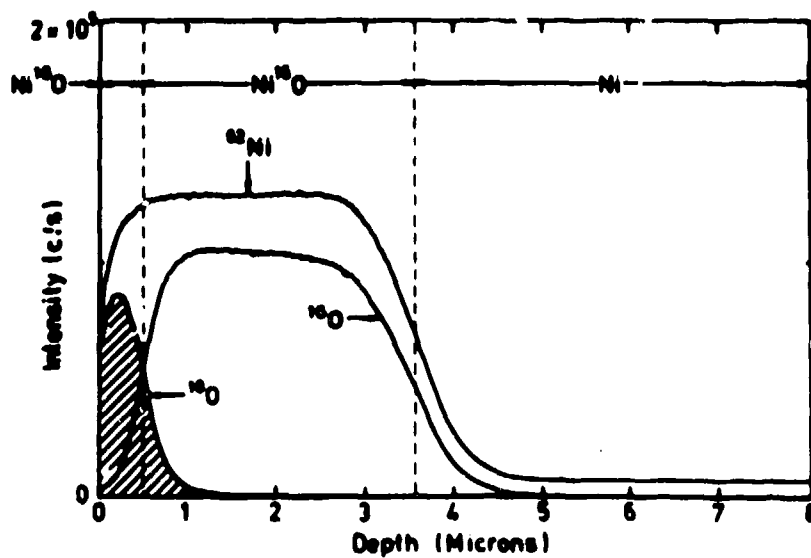
Oxidation of Dilute Ni-Cr Alloys

Small alloying additions of Cr to Ni increase the oxidation rate forming a Cr-doped NiO film (34,35). This is usually interpreted as being the result of Cr-doping increasing the Ni vacancy concentration in NiO and hence the Ni diffusion coefficient. At temperatures above about 1100°C, where lattice diffusion dominates such a doping effect is indeed consistent with the Ni diffusion data (Fig. 4). However, at lower temperatures, where grain boundary diffusion dominates, the interpretation is not so straightforward for two reasons. First, the addition of even as little as 0.1% Cr is sufficient to cause the formation of a duplex film structure. Second, the diffusion experiments (Fig. 4) indicate that Cr decreases the diffusivity of Ni in NiO grain boundaries.

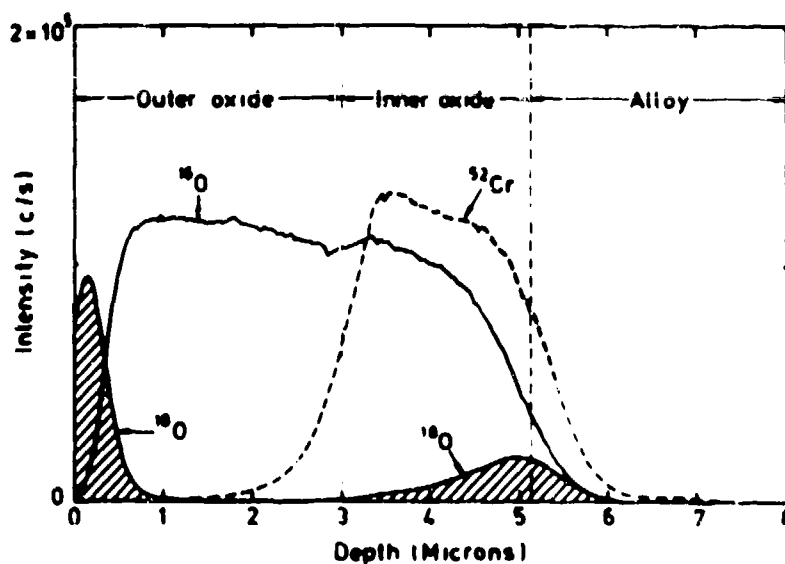
Some useful information concerning transport processes in growing films can be obtained by sequential oxidation using different oxygen isotopes; usually $^{16}\text{O}_2$ followed by $^{18}\text{O}_2$. Recently, experiments of this type have been carried out at Harwell to compare the behaviour of 'pure' Ni and Ni-0.1% Cr alloy at 700°C in oxygen (36). Some typical examples of isotope distributions in the oxide films measured by SIMS after $^{16}\text{O}_2/^{18}\text{O}_2$ sequential oxidation are presented in Fig. 10.

When 'pure' nickel was oxidised sequentially, in $^{16}\text{O}_2$ followed by $^{18}\text{O}_2$, the heavy isotope was found only near the oxide/gas interface (Fig. 10a). This is to be expected since film growth is occurring by the outward transport of Ni through NiO and new oxide units are formed at the outer surface of the film. There is little, if any, ^{18}O in the rest of the film, which is also to be expected from the low diffusivity of oxide ions in both the NiO lattice and grain boundaries (Fig. 1).

When Ni-0.1% Cr alloy was oxidised under the same conditions the parabolic rate constant was about a factor of two greater than that of 'pure' nickel. The SIMS profiles through the films show that in this case the distribution of ^{18}O is very different (Fig. 10b). As in the case of 'pure' NiO there is some ^{18}O incorporated near the oxide/gas interface, but in addition ^{18}O is also incorporated near the metal/oxide interface. Thus the films on Ni-0.1% Cr grow both by the outward transport of Ni and by the inward transport of oxygen; the oxygen transport occurring by a mechanism which allows negligible exchange of oxygen with the lattice. This could be either a direct interstitial defect mechanism, or transport by O_2 molecules in pores. The Cr profile shows that the Cr is located only in the inner part of the film, which is to be expected from the low diffusivity of Cr in both the NiO lattice and grain boundaries (Fig. 3). The areas under the outer and inner ^{18}O distributions are in the same ratio as the outer and inner oxide film thicknesses (as defined by the Cr distribution). Therefore, the inward oxygen transport accounts completely for the growth of the inner layer of the duplex film. Similar observations have been reported in the oxidation of many alloys (23). The inward oxygen transport is often attributed to oxygen grain boundary diffusion through the film. This is, however, not supported by the oxygen diffusion measurements (Fig. 1) which indicate that oxygen grain boundary diffusion is several orders of magnitude too slow to account for inward oxygen movement (it would have to be



Ni oxidised 5h $^{16}\text{O}_2$ and 2h $^{18}\text{O}_2$ at 700°C



Ni 0.1% Cr oxidised 5h $^{16}\text{O}_2$ and 2h $^{18}\text{O}_2$ at 700°C

Figure 10 - SIMS depth profiles through NiO films grown for 5 h in $^{16}\text{O}_2$ and then 2 h in $^{18}\text{O}_2$ in 1 atm oxygen at 700°C (36). (a) Pure Ni. (b) Ni 0.1% Cr alloy.

approximately equal to the Ni grain boundary diffusion coefficient). Furthermore, this would not explain the lack of oxygen penetration through the film grown on 'pure' nickel. The most likely transport path for oxygen is as O_2 gas molecules along fissures which develop only in the oxide on the Cr-containing alloy. However, such fissures have never been observed directly and the mechanism by which they might be generated is uncertain (23,27).

The increased oxidation rate of the Cr-containing alloy cannot easily be reconciled with the observation that Cr-doping inhibits the diffusion of Ni in NiO grain boundaries (Fig. 4). If we assume that the Cr in the inner layer reaches its equilibrium segregation to NiO grain boundaries and that the grain size is about $0.1 \mu m$ then the Cr/Ni ratio in the grain boundaries is estimated to be about 6×10^{-2} , which should be sufficient to block the boundaries. However, Cr is soluble in the NiO lattice and its diffusion coefficient is very low ($\sim 3 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ at 700°C , from Fig. 3). Equilibrium of Cr between grain and grain boundary could therefore take as long as 100 days at 700°C even for $0.1 \mu m$ grains. Thus the distribution of Cr between grains and grain boundary is unknown both in the inner layer of oxidation film and in the diffusion experiments. With such uncertainties it is not feasible to compare directly the diffusion and oxidation results.

Conclusions

There is much evidence (both direct and indirect) to indicate that short-circuit diffusion, particularly along grain boundaries, in oxide films has a dominant influence on oxidation processes at intermediate and low temperatures.

The experiments' data for dislocation and grain boundary diffusion are most extensive for NiO. The data cover self-diffusion (Ni and O), impurity diffusion (Co, Cr and Ce) and the influence of impurities (Co, Y and Cr). The diffusion data are supported by the results of atomistic simulations of grain boundaries in NiO. The atomistic calculations suggest a mechanism by which higher valency cations at oxide grain boundaries can block grain boundary diffusion by trapping vacancies. Diffusion data for Cr-doped NiO support this mechanism, but those for Co- and Y-doped NiO do not. This may be due to the lack of control over the distribution of dopant in the different specimens.

Lattice diffusion is usually found to be too slow by several orders of magnitude to account for the rate of growth of slow-growing oxide films. This has been taken to indicate the dominant influence of short-circuit diffusion. In the case of NiO the grain boundary diffusion measurements show that the relevant short-circuit is the outward diffusion of Ni along NiO grain boundaries.

The influence of Y, Co and Cr on the rate of Ni oxidation is not simply correlated with the influence of these impurities on grain boundary diffusion experiments. This is because the distribution of the impurities is important in both the oxidation and diffusion experiments and is usually not known. (Further complications arise from the influence of impurities on grain size, as well as diffusivity, and the formation of duplex film structures.) The system which has been studied most from the microstructural point of view is $\text{CoO}_2\text{-NiO}$. Here, microanalysis has shown that in part of the film all NiO boundaries contain Co at a level which is expected to block grain boundary diffusion and the oxidation experiments are consistent with this hypothesis. Thus it appears that the blocking mechanism is probably correct, but that a large excess of these relatively

insoluble and immobile impurities is required in order to ensure blocking of a sufficiently large fraction of grain boundaries in the film.

The addition of only 0.1% Cr to Ni is sufficient to cause the formation of a duplex film with the inner layer growing by inward oxygen transport. This inward transport is too fast to be accounted for by oxygen diffusion along grain boundaries or dislocations and is probably due to direct penetration of O_2 gas along fissures induced by the Cr impurity. However, the fissures have not been positively identified and their mechanism of formation, if they do exist, is unknown.

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References

1. A. Athinson, *Solid State Ionics*, **12** (1984) 309.
2. A. Athinson, *J. Phys. Paris Colloque C4*, **46** (1985) 379.
3. A. Athinson and A.D. Le Claire, in *Dislocations 1984*, Editors: P. Veyssi  , L. Hulin and J. Costain, (Editions des CMS, Paris, 1984) 233.
4. A. Athinson and R.I. Taylor, *Philos. Mag. A*, **39** (1979) 381.
5. A. Athinson and R.I. Taylor, *Philos. Mag. A*, **43** (1981) 979.
6. A.P. Sutton and V. Vitek, *Philos. Trans. Roy. Soc.*, **309** (1983) 1.
7. D.N. Duff and P.V. Tashor, *Philos. Mag. A*, **47** (1983) 817.
8. J.W. Greenbach and V.S. Stubican, *J. Amer. Ceram. Soc.*, **66** (1983) 191.
9. M.L. Peter sen, in *Grain Boundary Structure and Kinetics*, (ASM, Metals Park, Ohio, 1980) 309.
10. A. Athinson and R.I. Taylor, in *Transport in Non-stoichiometric Compounds*, Editors G. Simhovich and V.S. Stubican, (Plenum, New York, 1983) 283.
11. D.N. Duff and P.V. Tashor, Report TP 1155, Harwell Laboratory, Oxon, U.K., 1986.
12. J. Robier and H.P. Pels, *Philos. Mag. A*, **52** (1985) 461.
13. C. Dubois, C. Monty and J. Philibert, *Philos. Mag. A*, **46** (1982) 419.
14. A. Athinson, F.C.M. Tomer and C. Monty, in *Transport in Non-stoichiometric Compounds*, Editors G. Simhovich and V.S. Stubican, (Plenum, New York, 1983) 359.
15. A. Athinson and R.I. Taylor, *J. Phys. Chem. Solids*, **47** (1986) 315.
16. M.R. Motis, B. Jander and D.B. Williams, in *Grain Boundary Phenomena in Electronic Ceramics*, Editors L.N. Levinson and D.C. Hill, (Am. Ceram. Soc., Columbus, 1981) 91.
17. K. Hashino and M.L. Peter sen, *J. Phys. Chem. Solids*, **45** (1984) 963.
18. A.T. Chadwick and R.I. Taylor, *Solid State Ionics*, **12** (1984) 343.
19. A.A. Moos, S.J. Br     and L.J. Nevicki, *Oxidation of Metals*, **24** (1985) 115.
20. A. Athinson, D.P. Moon, D.V. Smart and R.I. Taylor, *J. Mater. Sci.*, **21** (1986) 1747.
21. A. Athinson and R.I. Taylor, (to be published).
22. C. Wagner, *Z. Phys. Chem.*, **21** (1933) 25.
23. A. Athinson, *Rev. Mod. Phys.*, **47** (1985) 437.

24. M.M. Shad, W.V. Smelter and J.D. Sabury, J. Electrochem. Soc., 122 (1975) 1493.
25. D. Caplan, H.J. Graham and H. Cohen, J. Electrochem. Soc., 119 (1972) 1208.
26. A. Atkinson, R.I. Taylor and A.E. Hughes, Philos. Mag. A, 43 (1982) 823.
27. R.N. Rhines and R.G. Connell, J. Electrochem. Soc., 124 (1977) 1122.
28. H.J. Graham and H. Cohen, J. Electrochem. Soc., 119 (1972) 879.
29. A.A. Moore and S.J. Rothman, Solid. Met., 24 (1983) 123.
30. A.T. Chodwick and R.I. Taylor, Solid State Ionics, 12 (1984) 343.
31. A.T. Chodwick and R.I. Taylor, in International Conference on Metallic Corrosion, Toronto, Canada, (1984) 481.
32. A.T. Chodwick and R.I. Taylor, J. Microscopy, 144 (1983) 221.
33. D.P. Mann, to be published.
34. F.H. Scott, Ph.D. Thesis, University of Manchester, (1976).
35. H.V. Atkinson, Oxidation of Metals, 24 (1983) 177.
36. D.W. Smart, to be published.
37. P. Refetad, Oxidation of Metals, 24 (1983) 265.